UNIVERSITI PUTRA MALAYSIA

MEASUREMENT OF THERMAL DIFFUSIVITY AND THERMAL EFFUSIVITY OF SOLID AND LIQUID USING PHOTOACOUSTIC TECHNIQUE

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By

TEH EE PHING

Thesis Submitted in Fulfilment of the Requirement of the Degree of Master of Science in the Faculty of Science and Environmental Study Universiti Putra Malaysia

June 2001

To my parents
and Lee Lee

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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June 2001

Chairman: **Associate Professor W. Mahmood Mat Yunus, Ph.D.**

Faculty: **Science and Environmental Studies**

The capability of photoacoustic technique in thermal diffusivity measurement has attracted a lot of interest lately. In the experiment, the open photoacoustic cell (OPC) technique was applied for thermal diffusivity measurement on solid materials such as metal, superconductors and soft ferrites. The photoacoustic signal amplitude was captured as a function of modulated frequency and the characteristic frequency, f_c, of each sample is computed. Thermal diffusivity was calculated based on the f_c and the sample thickness. The way that thermal diffusivity value behaves towards the change of dopant concentration were then investigated. Generally, the thermal diffusivity value measured were between 0.19 to 0.99 cm^2/s.

The second part of the work concentrated on liquid materials. By applying the basic theoretical approach and redesigning the OPC sample cell, the thermal effusivity value of liquid samples were able to be determined. The samples chosen were distilled water,

engine oil, lubricant, edible oil and creamy consumer products. The measured value was in a good agreement with the reported values previously published. The technique was feasible in obtaining thermal effusivity ranged from 0.042 to 0.159 $Ws^{1/2}/(cm^{2}{}^{\circ}C)$.

Thirdly, for liquid samples with low boiling point such as acetone, methanol and ethanol solvents, the PA technique was used to monitor its evaporation time. The sample of interest was placed in a 13.57 mm^3 container heated by a 30 mW He-Ne laser beam. As expected, the evaporation time were found to be inversely proportional to the respective boiling points.

The fourth part of the work focused on investigation on the protonation process in polyanilines, a kind of conducting polymer. The photoacoustic spectroscopy was obtained where the optical absorption spectrum was plotted against photon energy. Other then this, the Fourier Transform Infrared (FTIR) spectra, thermal diffusivity and scanning electron microscope (SEM) diagram were also examined. Generally, it was found that the formula structures before and after protonation were almost similar except the ptotonated polyaniline exhibited higher thermal diffusivity value.

The final part of the work was mainly on application of the phase shift approach against chopping frequency of the PA technique. The behavior of phase change with sample thickness was investigated. Later, the carrier transport properties of silicon wafer was measured based on the approach. The parameters examined were the surface recombination velocity and diffusion coefficient.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENGUKURAN PEKALI RESAPAN TERMA DAN EFFUSIVITI TERMA UNTUK PEPEJAL DAN CECAIR DENGAN TEKNIK FOTOACOUSTIK

Oleh

TEH EE PHING

Jun 2001

Pengerusi: **Prof. Madya W. Mahmood Mat Yunus, Ph. D.**

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Kebolehan teknik fotoakustik dalam pengukuran pekali resapan terma telah menarik minat para penyelidik kebelakangan ini. Dalam kajian ini, teknik fotoakustik sel terbuka (OPC) digunakan untuk pengukuran pekali resapan terma pada bahan pepejal seperti logam, superkonduktor and ferit. Magnitud isyarat fotoakustik telah diukur sebagai fungsi frekuensi termodulasi dan frekuensi kritikal, f_c, setiap sampel dikira. Pekali resapan terma kemudian dapat diperolehi berasaskan pada f_c dan ketebalan sampel. Perubahan nilai pekali resapan terma dengan perubahan ketumpatan pendopan telah pun diselidik. Secara amnya, pekali resapan terma yang dikaji berada dalam julat 0.19 hingga 0.99 cm^2/s.

Bahagian kedua dalam kajian ini bertumpu pada bahan cecair. Dengan menggunakan teori asas fotoakustik dan merekabentuk semula sel sampel OPC, nilai effusiviti terma untuk sampel cecair ditentukan. Antara sampel yang dipilih adalah air suling, minyak enjin dan bahan pengguna berbentuk krim. Nilai yang diukur didapati amat mendekati

nilai yang dilaporkan oleh penyelidik sebelum ini. Teknik ini berkemampuan untuk memperoleh effusiviti terma dalam julat 0.042 ke 0.159 $Ws^{1/2}/(cm^2 °C)$.

Ketiga, untuk sampel cecair dengan takat pengewapan rendah seperti aceton, metanol dan etanol, teknik PA telah dieksplotasikan untuk pemantauan masa pengewapan. Sampel cecair dimasukkan dalam suatu sel dengan isipadu 13.57 mm^3 dan dipanaskan dengan alur laser 30 mW. Masa pengewapan didapati berkadar songsang dengan takat pengewapan cecair masing-masing.

Bahagian keempat kajian ini bertumpu pada proses pemprotonan sejenis polimer konduktor iaitu *polyanilines*. Spektroscopi fotoakustik telah diperolehi di mana spektrum penyerapan optik telah diplotkan melawan tenaga foton. Selain daripada ini, spectra Infra Merah Fourier Transform (FTIR), pekali resapan terma dan mikroskop pengimbas elektron (SEM) telah juga dikaji. Amnya, telah didapati bahawa struktur formula sebelum dan selepas *protonation* adalah hampir sama melainkan *polyaniline* selepas protonation mempunyai pekali resapan terma yang lebih tinggi.

Bahagian terakhir kajian ini mengkaji pendekatan fasa melawan frekuensi dalam teknik PA. Sifat perubahan fasa dengan penukaran ketebalan sampel telah dikaji. Kemudian, sifat angkutan pembawa pada kepingan silikon diukur berdasarkan pendekatan tersebut. Antara parameter yang diselidik termasuklah halaju penyantuman permukaan dan pekali resapan.

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I gratefully acknowledge the award of the PASCA Scholarship from the Universiti Putra Malaysia, which enable me to undertake this work.

Last but not least is the support and encouragement from my beloved parents and Lee Lee. Their belief and patience have brought this study into success.

I certify that an Examination Committee met on 13th June 2001 to conduct the final examination of Teh Ee Phing on his Master of Science thesis entitled "Measurement of Thermal Diffusivity and Thermal Effusivity of Solid and Liquid Using Photoacoustic Technique" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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Date: 15 AUG 2001

The thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science.

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Date: 13 SEP 2001

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I declare that this thesis has not been previously or concurrently submitted for any other degree at UPM or other institutions.

(Teh Ee Phing)

Date 14 April 2001

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CHAPTER 1

INTRODUCTION

The Brief Historical Background

The photoacoustic effect and spectroscopy concept as cited by Wood (1992) were based on the first reported publication by the Alexander Graham Bell in the year of 1880. He placed a sample in an air filled cell and he observed that when a beam of modulated sunlight shinning onto a sample surface, a sound could be heard through a hearing tube attached to the cell. After Bell, no significant progress was found in the photoacoustic field until 1970, the photoacoustic and photothermal research again gained interest due to the invention of some advanced scientific apparatus. Improvement in such apparatus enabled detection with higher signal-to-noise ratio and therefore increased the sensitivity of the experiments. Three major improvement were:

1. The development of intense light sources; such as lasers, dye lasers and high pressure arc lamps, such as xenon lamps.
2. The development of sensitive detection equipment; such as condenser and electret microphones and piezoelectric detectors.
3. The development of more sensitive signal processing equipment; such as filters, phase sensitive detectors and lock-in amplifiers.

The first known use of a laser to be the light source in photoacoustic as cited by Wood. (1992) was in 1968, by Kerr and Attwood. They applied it in a gas photoacoustic system. This system was later developed by other research groups. Kreuzer and Patel (1971) and Goldan and Goto (1974) improved the signal to noise ratio obtained from a gas phase PA cell by developing a multi-pass cell. Later, Kreuzer et al. (1972) applied this system into practical problem such as the detection of atmospheric pollutants. One of the most renowned theory for photoacoustic spectra for solid sample was then published by Rosencwaig in 1973. Three years later, Rosencwaig and Gersho (1976) published the famous 1-dimentional theory, known as the R-G theory which has served as the basis of most of other theories on microphonic photoacoustic detection for a solid sample.

The Basic Concept of Photoacoustic Effect

The basic concept of the photoacoustic effect is that a sample is placed in an enclosed cell which is filled with a gas. The sample is then heated with a periodically modulated heating source. A microphone placed in the cell detects the pressure variations in the gas which are caused by periodic heat flow from the sample to the gas.

By examining the effect in detail, the absorption of photons by the molecules of a gas sample may induce a large variety of effects. The excited level may lose its energy by radiation processes, such as spontaneous or stimulated emission, and by radiationless collisional deactivation, which always channels at least part of the absorbed energy into the translational degrees of freedom. If the excitation energy is high enough, direct photochemical decomposition of the excited molecule can be achieved. In the case of fundamental vibration excitation, radiative emission and chemical reactions do not play an important role, because the radiative lifetime of vibrational levels is long compared with the time needed for collisional deactivation at ordinary pressures and the photon energy is too small to induce reactions. However, in the case of multiphoton and electronic excitation, chemical reaction processes may compete efficiently with collisional deactivation. This may also be true for the emission of radiation from electronic levels. These competing processes are illustrated in Figure 1.1.

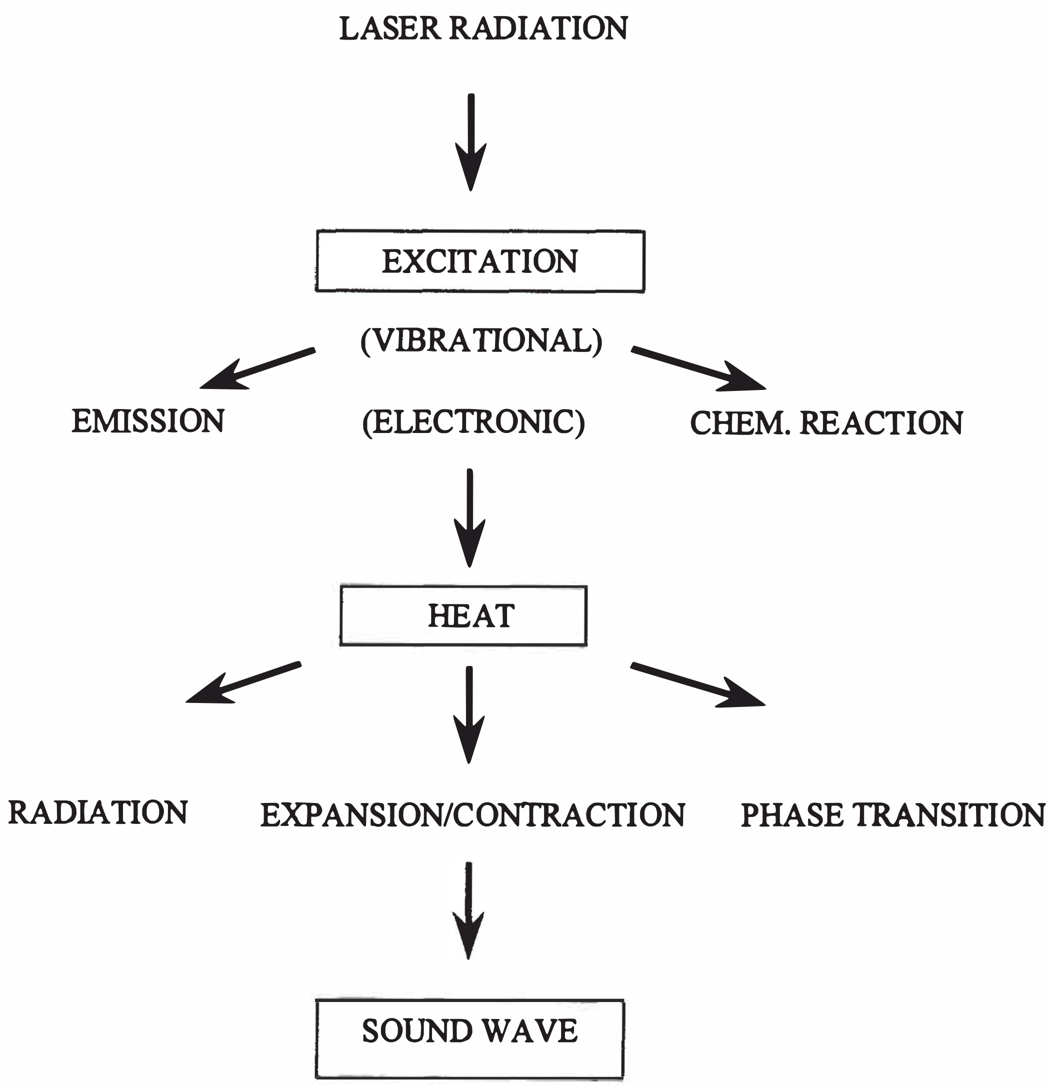

Figure 1.1: Transformation of Photon Energy into Heat and Photoacoustic Signal.

The photoacoustic spectroscopy or PAS is different than the conventional techniques in the sense that the earlier technique measured the energy absorbed by the material as a result of its interaction with the photon beam. There are several advantages of photoacoutics as a form of spectroscopy. Since absorption of modulated optical and electromagnetic radiation is required before a photoacoustic signal can be generated, light that is transmitted or elastically scattered by the sample is not detected and therefore does not interface with the inherently absorptive PAS measurements. The insensitivity to scattered radiation also permits investigation on optical absorption data on highly light-scattering materials such as powders, amorphous solids and gels. Secondly, it is capable on obtaining optical absorption spectra on completely opaque to lights-transmitted materials since the technique does not depend on the detection of the photons. Thirdly, it is capable in performing nondestructive depth-profile analysis of absorption as a function of depth into a material. As the result, photoacoustic has already found many important applications in the research and characterization of the materials. Photoacoustic studies are performed on all types of materials, inorganic, organic and biological on all the three matter states which includes gas, liquid, and solid. Listed below are some other attractive features of the photoacoustic spectroscopy:

1. Requires minimal sample preparation.
2. Application on broad range of material such as gases, liquids, solids, powders, gel, thin film and etc.
3. Application on wide range of photothermal detection methods.
4. It is always a non-destructive method.

The Present Work

For the present work, two different photothermal techniques i.e. open photoacoustic cell and closed photoacoustic cell were used to investigate the thermal properties of solid and liquid materials. Other than thermal characterization, application on optical absorption spectra for conducting polymer and carrier transport parameter of semiconductor was also done. The objective of each different experiment is summarized as below:

1. To measure the thermal diffusivity value of various solid samples by using the open photoacoustic cell (OPC) technique. The thermal diffusivity, α, is defined as $\alpha = k/\rho c$, where k is the thermal conductivity, ρ is the density and c is the specific heat at a constant pressure. The measurement were performed on aluminium, superconductor materials($Bi_2Pb_{0.6}Sr_2Ca_{2-X}M_XCu_3O_\delta$; M= Sn, V and Y) and soft ferrites ($MgO_{0.30-X}CuO_{0.20}ZnO_XFe_2O_{3(0.5)}$ and $MgO_XZnO_{0.5-X}Fe_2O_{3(0.5-\delta)}$).

2. To measure thermal effusivity values of various liquid samples by photoacoustic technique. Thermal effusivity is an important thermophysical property, defined as $e=(k\rho c)^{1/2}$. It could also be related with the thermal diffusivity with the expression $e = k/\sqrt{\alpha}$. It measures the sample's ability to exchange heat with the environment. The samples measured including distilled water, glycerol, engine oil, lubricant, various edible oil and creamy samples.

3. To monitor liquid evaporation time by photoacoustic technique. The samples used were solvent such as acetone, methanol and ethanol.

4. To investigate optical absorption spectra of polyanilines. The spectra before and after the process of protonation were captured applying photoacoustic spectroscopy (PAS). The FTIR spectroscopy spectrum and the thermal diffusivity values were also analyzed.

5. To obtain carrier transport parameters of Si semiconductor using OPC technique. The surface recombination velocity and diffusion coefficient of silicon wafer were obtained using this technique.